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Room temperature H_2S micro-sensors with anti-humidity properties fabricated from NiO-In_2O_3 composite nanofibers

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NiO-In_2O_3 composite nanofibers are synthesized via electrospinning and calcining techniques. Micro-sensors are fabricated by sputtering Pt electrodes on Si chips to form sensor substrates, and then spinning the NiO-In_2O_3 composite nanofibers onto the sensor substrate surface. The as-fabricated micro-sensors exhibit excellent H_2S sensing properties at room temperature. The sensitivity of the micro-sensors is up to 6 when the sensors are exposed to 3 μL/L H_2S, and the corresponding response and recovery times are 14 and 22 s, respectively. The micro-sensors also exhibit high selectivity and good stability. Especially, the micro-sensors can operate at various humidity conditions. The sensitivity of the micro-sensors is 3.8 to 3 μL/L H_2S at 75% relative humidity. These characteristics make the micro-sensors good candidates for practical H_2S sensors with high performance.

gas sensors, nanofibers, micro-sensors, metal oxide semiconductors, nanomaterials

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Over a period of four decades, metal oxide semiconductor (such as SnO_2, ZnO, In_2O_3 and TiO_2) based sensors have been under extensive investigation due to their applications in industrial and domestic sectors [1–5]. Semiconductor sensors work on the change of resistance to detect target gases. Particularly, based on the reaction between gas molecules and oxygen species, the potential barrier in the semiconductors is reduced by releasing electrons to the conduction band, and the sensor response can be obtained by comparing the subsequent change of resistance [6]. Among the sensing semiconductors, indium oxide (In_2O_3) is an important n-type III–V semiconductor with a band gap of 3.6 eV, which has been widely used for the detection of both oxidizing gases (e.g. O_3 and NO_x) and reducing gases (e.g. CO, H_2S and H_2) [7]. Especially, with various composites and nanostructures, In_2O_3-based sensors exhibit a versatile sensing performance in different conditions.

Hydrogen sulfide gas, which is frequently generated from sewage, rubbish dumps, as well as chemical producing processes, has strong toxicity, and has become an important research target on solid-state gas sensors in recent years. Hitherto, H_2S sensors, which are based on semiconducting oxides like SnO_2, In_2O_3, and WO_3, have been widely reported [8], but their performance still needs to be improved for various application demands. Recent investigations have shown that one-dimensional In_2O_3 nanomaterials exhibit H_2S sensitivity at low temperatures [9]. However, the investigations were only based on side-heating sensors. The grinding and coating steps in the fabrication process of the side-heating sensors unavoidably damage the structure and morphology of the sensing nanomaterials [9]. Therefore, the real performance of one-dimensional In_2O_3 nanomaterials is still yet to be determined, and according to early reports, their properties are expected to be much better than the previously reported values [10].

Herein, we present micro-sensors based on NiO-In_2O_3 composite nanofibers. Micro-sensors are key components of functional integrated circuits for their small volume, low power-consumption, excellent consistency and good compatibility. The micro-sensors used in this study have flat

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activity areas, which are beneficial for the protection of the fiber structure [11–13]. And, the synthetic technique of electrospinning is unique in that it offers a relatively facile and versatile method for the large-scale synthesis of one-dimensional (1D) nanostructures that are exceptionally long in length, uniform in diameter, large in surface area, and especially diversified in composition [14–16]. The current micro-sensors exhibit excellent H_2S sensing characteristics. And the micro-sensors can also operate at various humidity conditions. The high sensing performance and anti-humidity properties of the micro-sensors suggest that the micro-sensors are good candidates for practical H_2S detection.

1 Experimental

All chemicals (analytical grade reagents) were purchased from Beijing Chemicals Co. Ltd. and used as received without further purification. The electrospinning process in the present experiment is similar to that described previously for metal oxide nanofiber synthesis [16]. The precursor solution was prepared by dissolving 0.42 g of $In(NO)_3 \cdot 4.5H_2O$ and 0.013 g of $Ni(CH_3COO)_2 \cdot 4H_2O$ into 10 mL of DMF/EtOH (with the weight ratio of 1∶1), and then stirred for 4 h. Then, 1 g of PVP was added to the solution with stirring for a further 6 h. The mixture obtained was delivered to a hypodermic syringe at a constant flow rate of 1.0 mL/h, and then electrospun by applying 16 kV at an electrode distance of 15 cm. A piece of flat aluminum foil was employed to collect the precursory jets.

Micro-sensors were fabricated by spinning NiO-In_2O_3 composite nanofibers on to the sensor substrate surface (Figure 1(a)). The substrates were prepared according to the following steps: (a) grow a SiO_2 (thickness of 2000 Å) layer on a Si-chip as an insulating layer, (b) sputter a platinum layer (thickness of 1800 Å) on the SiO_2 layer, (c) mask pattern transfer to the Si wafer by photolithography using a photoresist, (d) etch the platinum layer by reactive ion etching to form signal electrodes, and finally, (e) remove the photoresist. A top view (obtained using an optical microscope) and schematic representation of the electrode design of the micro-sensors are shown in Figure 1(b). The electrode width was 20 μm, and the sensor area was 600 μm× 200 μm. Sensing films were obtained by laying sensor substrates on the aluminum foil during the electrospinning process and spinning precursory jets for 4 h. And then, the substrates with jets were dried for 12 h at room temperature, and then annealed in a tube furnace with a rising rate of 1°C/min from room temperature for 3 h at 600°C. The substrates were then self-cooled down to room temperature again to form the final a NiO-In_2O_3 composite nanofiber-based micro-sensors. Figure 1(c) is a photograph of a socketed sensor.

The sensor performances were measured using a CGS-8 (Chemical Gas Sensor-8) intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China) (Figure 1(d)).

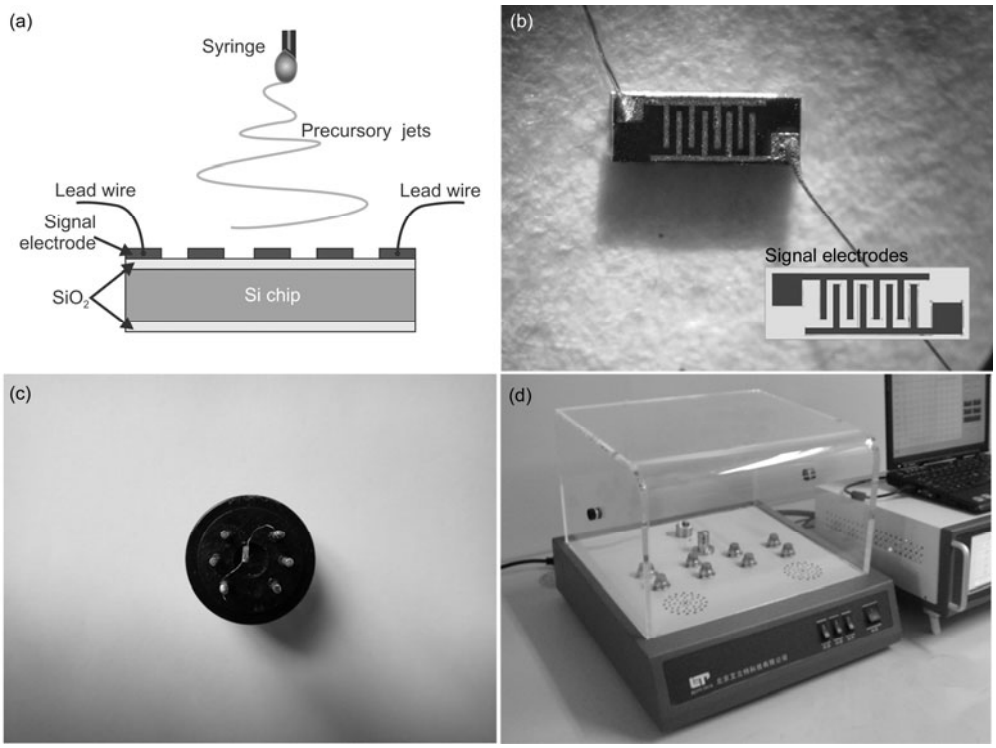

Figure 1 Fabrication process of the micro-sensors (a), a photograph of sensor substrates and its electrode design (b), a photograph of a socketed sensor (c), and a photograph of the sensing analysis system comprising eight micro-sensors (d).

Gas ambiences were obtained using a static test system [14,15]. When the resistances of the micro-sensors in the analysis system were stable, saturated target gas was injected into the test chamber (20 L in volume) by a micro-injector through a rubber plug. The saturated target gas was mixed with air by two fans in the analysis system. After the sensor resistances reached new constant values, the test chamber was opened to recover the micro-sensors in air. The whole experiment process was performed in a super-clean room with the constant humidity (25% relative humidity (RH)) and temperature (20°C) (which were also monitored by the analysis systems).

The humidity interference of the micro-sensors was studied by exposing the micro-sensors to the mixed gas of H_2S and humidity. The RH ambience of 75% RH (corresponding to NaCl) was obtained using a saturated salt solution as the humidity generation source [14].

The response value (R) was designated as $R=R_a/R_g$, where R_a was the sensor resistance in air (base resistance) and R_g was a mixture of target gas and air. The time taken by the sensor resistance to change from R_a to $R_a–90\%\times(R_a–R_g)$ was defined as response time when the target gas was introduced to the sensor, and the time taken from R_g to $R_g+90\%\times(R_a–R_g)$ was defined as recovery time when the ambience was replaced by air.

The crystal structures of the products were determined by X-ray powder diffraction (XRD) using an X-ray diffractometer (Siemens D5005, Munich, Germany). Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEOL JEM-2000EX microscope with an accelerating voltage of 200 kV.

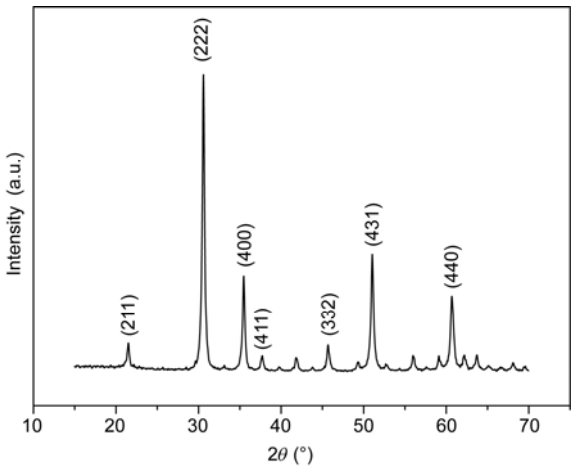

Figure 2 XRD pattern of the NiO-In_2O_3 composite nanofibers.

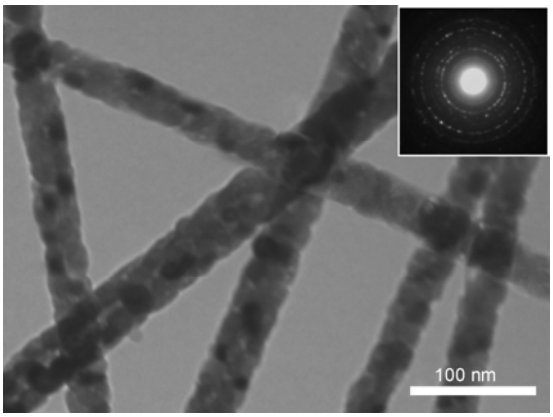

Figure 3 A TEM image and SAED pattern (inset) of NiO-In_2O_3 composite nanofibers.

2 Results and discussion

Figure 2 shows the XRD pattern of the NiO-In_2O_3 composite nanofibers. The diffraction peaks and their relative intensities match very well with those given by the JCPDS card no. 06-0416 for cubic In_2O_3. The crystallite size based on the XRD pattern is about 10 nm, which is estimated using Scherrer's formula. No peaks corresponding to NiO were observed, which is because of the very low rate of Ni in the In_2O_3 system.

Figure 3 shows a TEM image of the NiO-In_2O_3 composite nanofibers. The nanofibers consist of regular nanoparticles with an average diameter of about 12 nm. The properties of a gas sensing material strongly depend on its particle size, which has a great influence on the surface reaction between the sensing material and the gas molecules. According to a previous sensing theory [6], minimizing the particle diameter (D) will lead to a converging of the Schottky barriers, if the radius $r=D/2$ is in the range of the space-charge layer (about 10–30 nm). This means that with a further decrease of the radius, the depleted zones start to overlap and consequently the electrical properties are predominantly determined by the surface states. Therefore, a pronounced dependence of the sensitivity on the particle size is expected with enhanced sensitivity towards smaller particle sizes. However, some experimental results are not consistent with this theory because intense aggregation occurs among small nanoparticles [6]. In recent years, 1D nanostructures have been shown to avoid such aggregation, so the particle diameter-effect will be more prominent in 1D nanostructures [17]. The XRD and TEM results confirm that the current nanofibers consist of very small particles, which may eventually lead to a large response. Simultaneously, the high surface-to-volume ratios of the 1D nanomaterials can provide more sites for the adsorption of analyte molecules, and the web-like structure formed by the nanofibers on the sensor surface will also benefit for the sensing enhancement [14]. Therefore, the obtained NiO-In_2O_3 composite nanofibers are expected to exhibit a very high sensing performance due to these characteristics. The SAED pattern inset in Figure 3 shows that the NiO-In_2O_3 composite nanofibers are polycrystalline in structure.

The response and recovery speeds of chemical sensors

are dependent on the operating temperature of the sensors. Higher temperatures can accelerate the reaction speeds, leading to shorter response and recovery times. For nanoparticle-based sensors, their optimized operating temperature is around 300°C. Therefore, lots of dopants are needed to improve their reacting activation at low temperatures. However, 1D nanostructures can provide more active sites for gas adsorption, and thus lead to a very high sensitivity at low temperatures. The response and recovery characteristics shown in Figure 4 suggest that the micro-sensors exhibit a high sensitivity and quick response and recovery speeds at room temperature. The sensitivity is up to 6 when the sensors are exposed to 3 μL/L H_2S, and the corresponding response and recovery times are 14 and 22 s, respectively. Compared with many previous room temperature sensors [18], the present sensors exhibit a much higher sensitivity and shorter reaction times, and these results directly prove the high sensing performance of this type of micro-sensor.

The micro-sensor sensitivity versus H_2S concentration at room temperature is shown in Figure 5. With raising H_2S concentration, the sensor sensitivity rapidly increases. For instance, the sensitivities are about 11, 65, and 478 to 10, 100, and 1000 μL/L H_2S. The sensor reaches saturation at about 6000 μL/L (the sensitivity is about 710). These results indicate that the presented micro-sensors are more suitable for H_2S detection at low concentrations.

Furthermore, the micro-sensors were also exposed to different gases (100 μL/L) to reveal their selectivity at room temperature (Figure 6). The sensors show prominent sensitivity to H_2S, very low sensitivities to C_2H_5OH and CH_3OHCH_3, and almost no response to CH_3OH, NH_3, $C_6H_5CH_3$, C_6H_6, CH_4, H_2 and C_2H_2. These results suggest that the sensors exhibit a high selectivity and can be employed in various applications.

Figure 7 shows the response-recovery curves of the micro-sensors at different RH conditions. The sensitivity of the micro-sensors is decreased at higher RH condition. However, the micro-sensors can still detect well 3 μL/L H_2S in 75% RH condition. The sensitivity is about 3.8 to 3 μL/L H_2S at

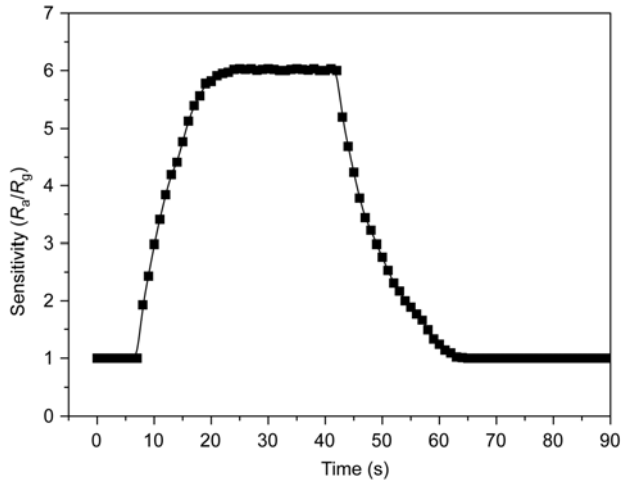

Figure 4 Response and recovery characteristics of the micro-sensors to 3 μL/L H_2S.

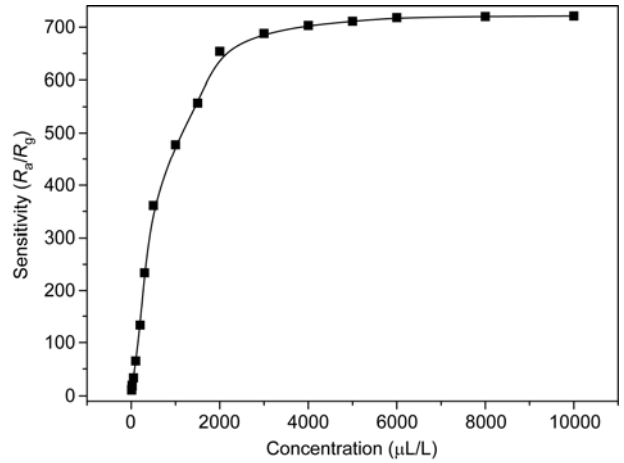

Figure 5 Sensitivities of the micro-sensors to different H_2S concentrations.

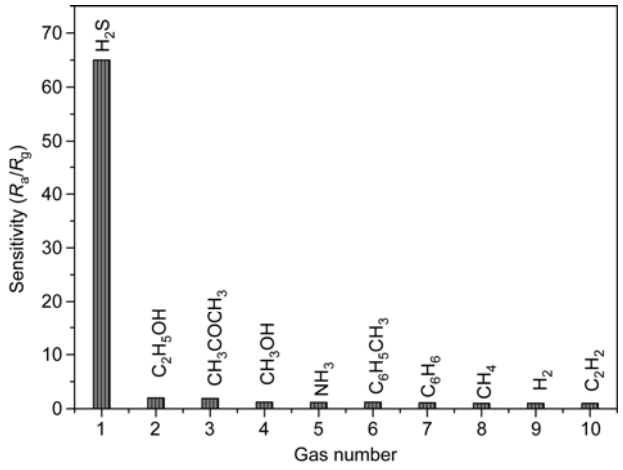

Figure 6 Sensitivities of the micro-sensors to 100 μL/L different gases.

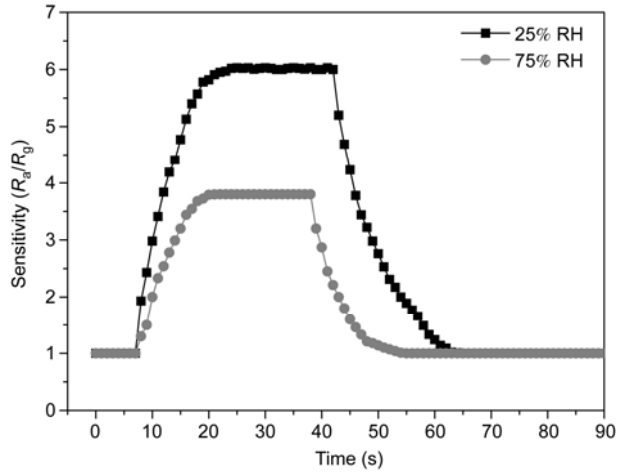

Figure 7 Response and recovery characteristics of the micro-sensors to 3 μL/L H_2S at different RH conditions.

75% RH, indicating the anti-humidity characteristics of the micro-sensors.

To test the stability of the as-fabricated micro-sensors, the sensors were exposed in air for 60 d, followed by measuring the sensitivities at various H_2S concentrations. As shown in Figure 8, there is an acceptable change in the sensitivities, proving a good stability of the micro-sensors.

For most metal oxide semiconductor sensors, their gas sensing response is based on the adsorption and desorption of the target gas molecules on the material surface. At high operating temperature, the interaction of the gas molecules and oxygen ions (O_2^-, O^- and O^{2-}) dominate the senor response, and the resistance change of the sensors can be explained by the capture and release of electrons from the conductance band of the sensing materials [19,20]. But for low temperature sensors, their sensing mechanism is quite different. In this case, the high H_2S sensing properties of the micro-sensors are related to the sulfuration reaction of the NiO-In_2O_3 composite nanofibers [9]. The reaction can be simply described as:

$$In_2O_3(s)+3H_2S(g)\rightarrow In_2S_3(s)+3H_2O\ (g)$$

$$In_2S_3(s)+9/2\,O_2(g)\rightarrow In_2O_3(s)+3SO_2(g)$$

Both of the two processes are spontaneous in thermodynamics [9], thus the trend of the sulfuration reaction will be weakened with increased operating temperature. This reaction can be considered to understand the high H_2S sensitivity of the current nanofibers at room temperature. The effect of Ni in the In_2O_3 system has been explained by Ivanovskaya et al. [21]. NiO is a p-type material. When a small amount of NiO is doped in an n-type material (such as In_2O_3 in this case), some hetero-contacts may form between the NiO and In_2O_3. It is represented that when the micro-sensors are exposed to the target atmosphere, the chemical species to be detected in the atmosphere can permeate into the interface of the p-n junction, and lead to changes in the electrical properties at the junction [6]. This model has been widely selected for the explanation of sensing enhancement brought about by p-type dopants in n-type materials such as Cu-ZnO, Ni-SnO_2, Co-In_2O_3 and Cu-SnO_2 systems. On the other hand, the response of the NiO-In_2O_3 micro-sensor to reducing gases at low temperatures may be caused by the participation of Ni^{III} ions in the analyte oxidation. Electronic exchange in the complex [H_2S-Ni^{III}] can lead to the reduction of nickel ions from Ni^{III} to Ni^{I}, resulting in the high H_2S sensing performance of our sensor. Additionally, taking into consideration the high surface-to-volume ratio, effective electron transport, and greatly reduced aggregation associated with the NiO-In_2O_3 micro-sensor, excellent H_2S sensing characteristics can be found.

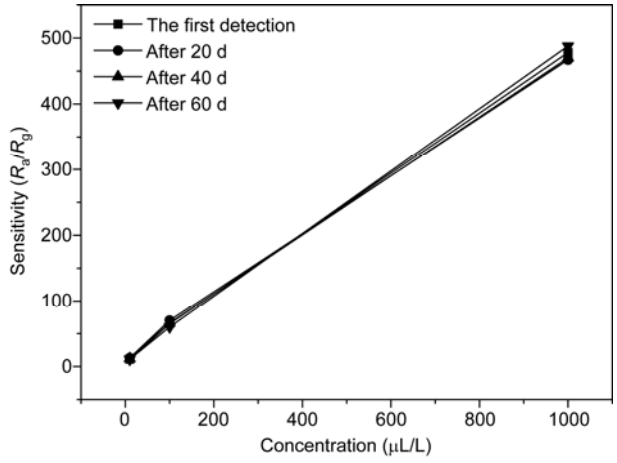

Figure 8 Sensitivities of the micro-sensors to 10, 100, and 1000 μL/L H_2S measured up to 60 days.

3 Conclusions

In summary, NiO-In_2O_3 composite nanofibers are synthesized through an electrospinning method. Micro-sensors are fabricated by spinning the nanofibers on to the surface of Si-based substrates. The as-fabricated micro-sensors exhibit excellent H_2S sensing properties such as high sensitivity, quick response and recovery, good selectivity, anti-humidity, and high stability. The results suggest that the micro-sensors can be employed for use as practical H_2S sensors with high performance.

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